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PAHs in Space: the Evidence and Implications.

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1. – Introduction.

An intriguing and exciting chapter of modern astrophysics was opened by GILLETT, FORREST and MERRILL in 1973 [1] with their discovery that some astronomical objects emitted a broad band which peaks near $3050\,cm^{-1}$ ($3.28\,\mu m$). In the ensuing years, astronomers around the world found that this was part of a family of infrared emission features which were emitted by a large number of very different types of astronomical objects. The other prominent, well-known bands, or features as they are often called, peak near 1610, «1310», 1160 and $890\,cm^{-1}$ (6.2, «7.7», 8.6 and $11.2\,\mu m$). They are broad, with a FWHH on the order of $(30 \div 50)\,cm^{-1}$ or more. The peak frequencies do not seem to vary by more than a few wave numbers from object to object except for the case of the «1310» cm^{-1} («7.7» μm) feature in which it can differ by as much as $50\,cm^{-1}$. Reviews of the ground breaking observations can be found in ref. [2, 3]. This lecture borrows heavily from ref. [4].

As the list of astronomical objects which emit these features grew, it became clear that the emission came from regions where ultraviolet radiation was impinging on vast areas of space in which dust was known to be present. Surprisingly, the age and history of the dust seemed to be unimportant. On the one hand, illumination from hot, UV-rich stars which had formed in—and emerged from—dense, dark dust clouds (age $\sim (10^6 \div 10^7)$ y) could excite the emission from the surface of the cloud. Examples of this type of object include H II regions and some reflection nebulae. On the other hand, similar spectra are emitted from some much younger, isolated objects known as planetary nebulae. These are stars near the end of their normal life which have produced copious amounts of dust during the past $(10^4 \div 10^5)$ y. This dust has a very different history and is much younger than the dust in dense clouds. During the late 1970s and early 1980s, the emission was detected from other galaxies as well. The intensities of the bands detected, however, were far greater than those which would be expected from the individual objects which comprised the galaxies such as planetary nebulae, reflection nebulae, H II regions and so on. The implication was that a substantial fraction of this extragalactic emission came from regions which were not associated with individual stars, but from the dark matter in the interstellar medium in these galaxies [5]. Subsequent observations of our galaxy, the Milky Way, by the Infrared Astronomical Satellite (IRAS) have shown that there are strips of interstellar IR-emitting clouds, known as the IR Cirrus, that lie slightly above and below the galactic plane which seem to emit these bands as well [6]. Obviously, understanding the source of this completely unexpected, yet widespread, phenomenon became an important problem in astrophysics.

As the number and variety of objects found to emit the features increased, identifying the carrier and determining the emission mechanism became the key challenges. During the seventeen years since their discovery, a number of models had been proposed to account for both aspects of the problem. Many of the models proposed up to 1984 are reviewed in ref. [7]. The comparable intensity of the $3050\,cm^{-1}$ ($3.28\,\mu m$) feature to those at lower frequencies and the close association with ultraviolet radiation led us to propose that the emission was due to the infrared fluorescence from molecule-sized emitters excited by the absorption of ultraviolet and visible photons [8, 9]. Although the carrier we initially proposed (molecules, frozen on 10 K dust grains) was incorrect, this excitation-emission mechanism is now generally accepted because of the important observations and analysis of the emission feature from reflection nebulae made by SELLGREN which showed that the ultraviolet and visible photon fluxes present were unable to sufficiently excite larger species to emit in the $3000\,cm^{-1}$ ($3\,\mu m$) region [10]. The idea, now gaining wide acceptance, that aromatic material may be the carrier of the features began with the suggestion made by DULEY and WILLIAMS in 1981 that they arise from vibrations of chemical groups attached to the aromatic moieties which make up small ($< 0.01\,\mu m$ radius) amorphous carbon particles [11]. Subsequently, LEGER and PUGET [12] and ALLAMANDOLA, TIELENS and BARKER [13] proposed that individual polycyclic aromatic hydrocarbon molecules (PAHs) were the band carriers.

The principal reason for this assignment was the suggestive, but not perfect, resemblance of the interstellar emission spectra with the infrared absorption spectra of PAHs in KBr pellets. This assignment was supported by the better match of the interstellar features with the vibrational spectra of chars and soots which are comprised of mixtures of polycyclic aromatic hydrocarbons [14]. The need to invoke emission from free molecules rather than from the aromatic building blocks of amorphous carbon particles was driven by the fluorescent nature of the emission. Energy deposited in a particular molecular structural unit of a larger particle or cluster is thought to become thermalized on time scales on the order of $(10^{-11} \div 10^{-13})$ s, many orders of magnitude shorter than the $(10^{-3} \div 10^{-2})$ s time scale appropriate for the emission of IR photons. Emission from molecular units in a particle implies extremely weak intermolecular coupling [15] and has yet to be demonstrated. This question is presently the matter of some debate.

The imperfect match between the IR spectra of PAHs with the interstellar emission bands has been taken to indicate that, rather than pure aromatic compounds being responsible, aromaticlike (or PAH-like) species are present in the interstellar medium. In many regions of the interstellar medium PAHs are expected to be ionized [13] and those containing less than about 20 carbon atoms are expected to be dehydrogenated [11-13].

In addition to the spectroscopic evidence, related observations support an aromatic hydrocarbon carrier as well. In planetary nebulae, the fraction of the IR emitted in the «1310» cm^{-1} («7.7» μm) feature, which is by far the most intense of the bands, is strongly correlated with the amount of carbon available [16]. As the carriers must be produced under harsh conditions in planetary nebulae, they must be carbon-rich compounds which are extremely stable. Finally, although there is some variation among the relative band intensities, the bands are correlated, implying that a single class of chemical species is responsible [16].

Apart from the «curiosity» value, why is the discovery of a previously unrecognized and surprisingly ubiquitous component of the interstellar medium important astrophysically? There are several reasons. Current estimates are that between 1 and 10% of all of the carbon in the Galaxy is in PAHs comprised of roughly 15 to, say, 500 carbon atoms [17]. The PAHs responsible for the IR features are thought to be more abundant than all of the other known interstellar, gaseous, polyatomic molecules combined [12, 13]. Their proposed ubiquity and high abundance has serious ramifications for other spectral regions. They may well contribute to the strong ultraviolet interstellar extinction, measured between 100 and 200 nm: the weak, diffuse, visible absorption bands [18-20] and the far-IR Cirrus [13, 21]. Similarly their influence on many physical processes may be profound [22]. They may comprise much of the carbon in meteorites [23] and be responsible for maintaining interstellar-cloud temperature [24], moderating interstellar-cloud chemistry [25] and contributing to the deuterium enrichment found in interplanetary dust particles and meteorites [26]. Comprehensive treatments of various aspects of the polycyclic aromatic hydrocarbon model can be found in ref. [27, 28].

In view of the previous paragraph, it is important to realize that precious little information is available on important properties of individual PAHs. For example, little is known about the spectroscopic properties of PAH ions and radicals from the UV through the IR. Other important, but poorly understood properties include photoionization cross-sections, electron capture cross-sections, cluster geometry, n-mer binding energies and so on. Recently, important information on fragmentation patterns of doubly ionized PAHs has become available [29, 30]. The carbon chemistry in the stellar atmospheres in which they are produced is just beginning to be modelled and poses significant chemical kinetic challenges [31, 32]. There is much to be done both experimentally and theoretically before the PAH model can be reliably extended from a means to account for certain observations to the point where it can be exploited as a probe of interstellar and circumstellar processes and conditions.

It is becoming increasingly apparent that the interstellar emission includes contributions from both free PAHs and carbonaceous particles as well [14, 33]. As amorphous carbon is primarily made up of randomly oriented clusters of PAHs, cross-linked and interconnected by saturated and unsaturated hydrocarbon chains, the infrared spectra of amorphous carbons and hydrogenated amorphous carbons should resemble spectra of PAH mixtures with some of the individual bands blurred out due to solid-state intermolecular interactions. If the H content is high, in addition to the aromatic features, aliphatic CH bands between 2950 and 2850 cm^{-1} (3.38 and 3.51 μm) and 1500 and 1400 cm^{-1} (6.67 and 7.14 μm) should become evident in the spectra of carbonaceous materials. The aromatic signature of small amorphous carbon particles and PAH clusters will be largely determined by the properties of the PAHs of which they are made. Individual bands overlap as the particles get larger and broad features are produced which may retain some substructure indicative of the individual PAHs. For still larger particles, bulk properties dominate and the broad components appear as substructure on a strong continuum. As with PAH molecules, the spectroscopic and physical properties of amorphous carbon must be studied in detail.

In this lecture the infrared spectroscopic evidence for interstellar PAHs will be reviewed. The spectroscopic properties of PAHs studied in salt pellets (rather than amorphous carbons) will be primarily used since a wealth of very detailed information is available (thanks to the sustained, dedicated effort of Prof. N. CYVIN and his colleagues at Trondheim University in Norway over many years) and molecule-sized emitters can account for many details of the interstellar spectra. Infrared spectra of amorphous carbon particles and carbonaceous films, synthesized to study the connections with interstellar carbonaceous material, are just now becoming available. The work of Bussoletti and co-workers ([34] and references therein) and Sakata and colleagues ([35] and references therein) is particularly noteworthy in this regard. A thorough review of the spectroscopic assignments, the excitation-emission mechanism and some astrophysical applications of the overall PAH model is given in ref. [17].

2. – The interstellar emission spectrum.

Infrared spectra of celestial objects are usually measured in narrow frequency ranges because the Earth's atmosphere is opaque in certain infrared regions and the most sensitive instrumentation is region specific. Consequently, although nearly complete mid-IR spectra have been published for only a few objects, detailed spectroscopic information is available in certain frequency ranges for many objects. Spectra have been measured in regions which are obscured by telluric H_2O using NASA's Kuiper Airborne Observatory which can operate a telescope at $(12 \div 14)$ km altitude. Observations in the $(2000 \div 1000)\,cm^{-1}$ $((5 \div 10)\,\mu m)$ region made in this aircraft have played a very important role in unraveling the mystery of the interstellar infrared emission bands. Reliable observations in the $(2500 \div 2100)\,cm^{-1}$ $((4 \div 4.8)\,\mu m)$ and $700\,cm^{-1}$ $(14\,\mu m)$ to lower-frequency regions must await spaceborne instrumentation. The former region is blocked by atmospheric CO_2 and the latter by a combination of CO_2 and the very rich H_2O rotation spectrum. Fortunately the

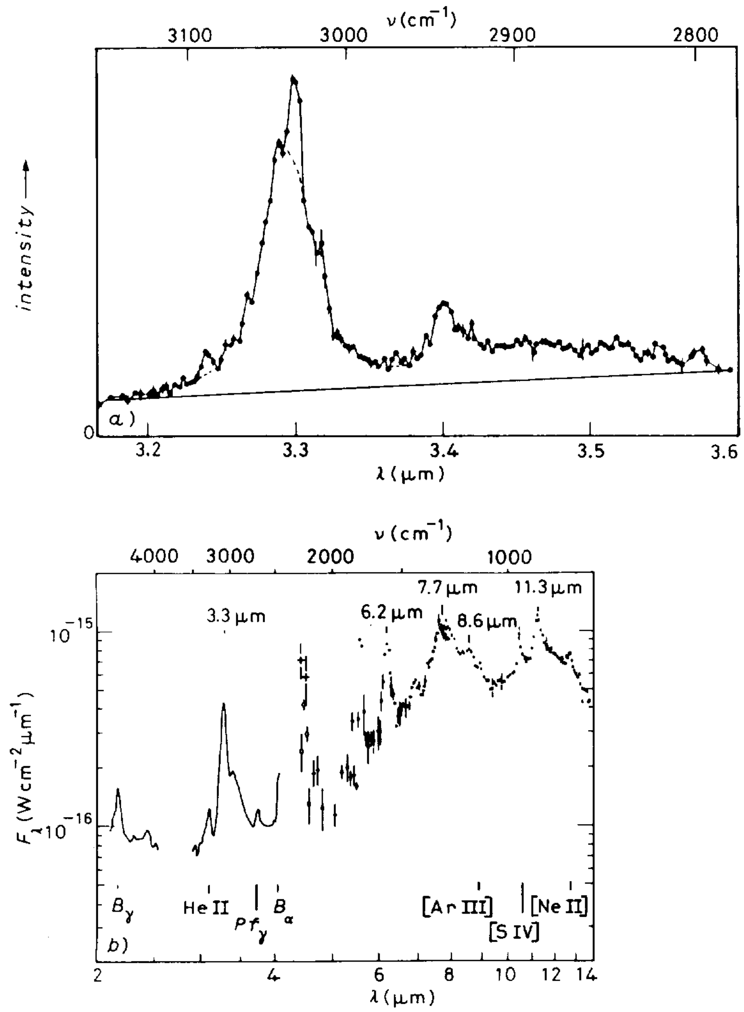

Fig. 1. – The infrared emission spectrum from the high-excitation planetary nebula NGC 7027. (*a*) from ref. [36], *b*) from ref. [37].).

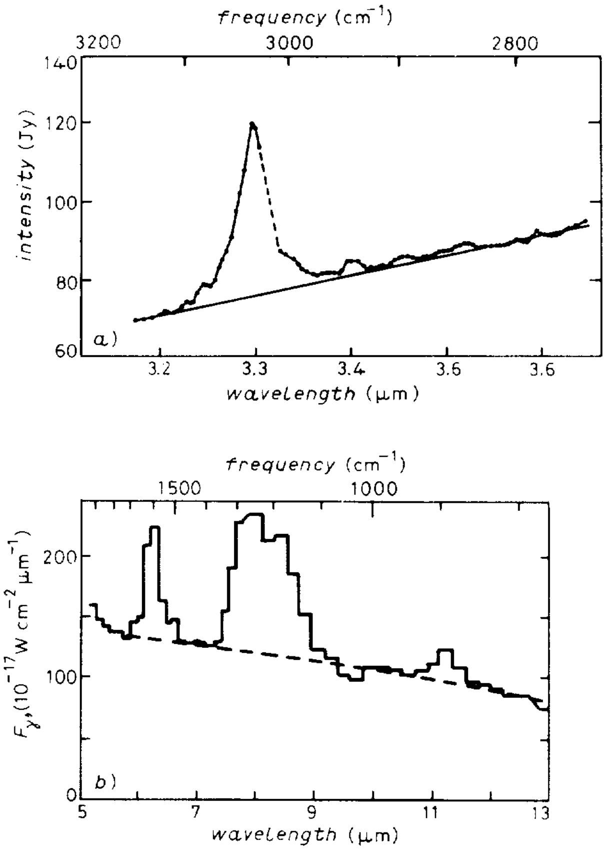

Fig. 2. – The infrared emission spectrum from the reflection nebula HD 44179, the Red Rectangle. (*a*) from ref. [38], *b*) from ref. [16].)

Infrared Space Observatory (ISO), an infrared satellite under construction by the European Space Agency (ESA), is planned to be launched in the early 1990s, and the Space Infrared Telescope Facility (SIRTF), a complementary infrared satellite at an earlier stage of development by the National Aeronautics and Space Administration (NASA) in the United States, is planned to be launched in the latter part of the 1990s.

Good examples of nearly complete mid-IR spectra are shown in fig. 1, 2 and 3*a*), *b*). In addition to the family of bands at 3050, 1610, «1310», 1160 and 890 cm^{-1} (3.3, 6.2, «7.7», 8.6 and 11.3 μm), these figures show that there are striking variations in the underlying continuum and small changes in the «1310» cm^{-1} («7.7» μm) band. Perusal of these figures also shows that there are 3 types of spectral components: major bands, minor (weak) bands and broad features. The broad features span roughly the $(3200 \div 2750)$ cm^{-1} $((3.13 \div 3.64)$ μm), $(2000 \div 1100)$ cm^{-1}

$((5 \div 9)\,\mu m)$ and $(900 \div 700)\,cm^{-1}$ $((11 \div 14)\,\mu m)$ regions. The band positions, widths and assignments are summarized in table I. In each of the following subsections, which focus on specific frequency regions, these will all be discussed in this order: the major bands first, the minor bands next, the broad components last.

TABLE I. – *Emission components: properties and assignments* (1).

ν (cm^{-1})	λ (μm)	FWHM (cm^{-1})	Assignment (2)
The major bands			
3040	3.29	30	aromatic C—H stretch ($v = 1 \rightarrow v = 0$)
1615	6.2	30	aromatic C—C stretch
$1315 \div 1250$	$7.6 \div 8.0$	$70 \div 200$	blending of several strong aromatic C—C stretching bands
1150	8.7	—	aromatic C—H in-plane bend
885	11.3	30	aromatic C—H out-of-plane bend for nonadjacent, peripheral H atoms
The minor features			
3085	3.24	—	overtone and/or combination involving fundamentals in the $(1810 \div 1050)\,cm^{-1}$ $((5.52 \div 9.52)\,\mu m)$ range
2995	3.34	—	overtone and/or combination involving fundamentals in the $(1810 \div 1050)\,cm^{-1}$ $((5.52 \div 9.52)\,\mu m)$ range
2940	3.4	«20»	aromatic CH stretch ($v = 2 \rightarrow v = 1$)
2890	3.46	—	overtone/combination band involving fundamentals in the $(1810 \div 1050)\,cm^{-1}$ $((5.52 \div 9.52)\,\mu m)$ range, aromatic CH stretch (high v), aliphatic CH stretch, ?
2850	3.51	—	aromatic CH stretch ($v = 3 \rightarrow v = 2$), aliphatic CH stretch, overtone/combination band involving fundamentals in the $(1810 \div 1050)\,cm^{-1}$ $((5.52 \div 9.52)\,\mu m)$ range
2810	3.56	—	aromatic CH stretch (high v), aldehydic CH stretch, overtone/combination band involving fundamentals in the $(1810 \div 1050)\,cm^{-1}$ $((5.52 \div 9.52)\,\mu m)$ range

TABLE I (*continued*).

1960 ÷ 1890	5.1 ÷ 5.3	30	combination of CH out-of-plane and in-plane bend,?
1785 ÷ 1755	5.6 ÷ 5.7	40	aromatic C—C stretch; overtone of 885 cm^{-1} (11.3 μm) band; carbonyl C=O stretch,?
1470 ÷ 1450	6.8 ÷ 6.9	30	aromatic C—C stretch, aliphatic CH deformation
840	11.9	—	C—H out-of-plane bend for doubly adjacent H atoms
790	12.7	—	C—H out-of-plane bend for triply adjacent H atoms
The broad components			
2940 3115 ÷ 2740 (*)	3.5 3.21 ÷ 3.65 (*)	— «300»	overlap of C—H stretching modes, shifted by anharmonic effects, with overtones and combinations of C—C stretch fundamentals in the (1670 ÷ 1250) cm^{-1} ((6 ÷ 8) μm) region, aliphatic CH stretch?,?
~ 1200 1810 ÷ 1050 (*)	~ 8.5 5.52 ÷ 9.52 (*)	«400»	blending of many weak aromatic C—C stretching bands
880 950 ÷ 740 (*)	12 10.5 ÷ 13.5 (*)	«160»	overlap of many aromatic C—H out-of-plane bending modes for nonadjacent as well as doubly and triply adjacent peripheral H atoms
red near-IR continuum			electronic transitions between low-lying levels in ionized and complexed PAHs and amorphous carbon particles
mid-IR continuum			quasi-continuum formed by overlapping overtone and combination bands

« » Value estimated from several published spectra.
(*) Rough limits of the feature.
(1) This table is extensively discussed in [17].
(2) When the assignment is not clear, several possible explanations are listed. The first seems most likely.

2·1. *The* (3200 ÷ 2700) cm^{-1} ((3.125 ÷ 3.704) μm) *region.*

2·1.1. The 3050 cm^{-1} (3.28 μm) major band. – Figures 1, 2, 3*a*) and 4 show that this region is dominated by the 3050 cm^{-1} (3.28 μm) emission band. This frequency is well known among IR spectroscopists as characteristic of the aromatic CH stretch [40-44]. This frequency played a strong role in Duley and Williams first suggestion of an aromatic carrier of the interstellar spectra in 1981 [11]. The 30 cm^{-1} FWHH is probably due more to nonradiative vibrational-energy redistribution times within an individual molecule rather than the overlapping

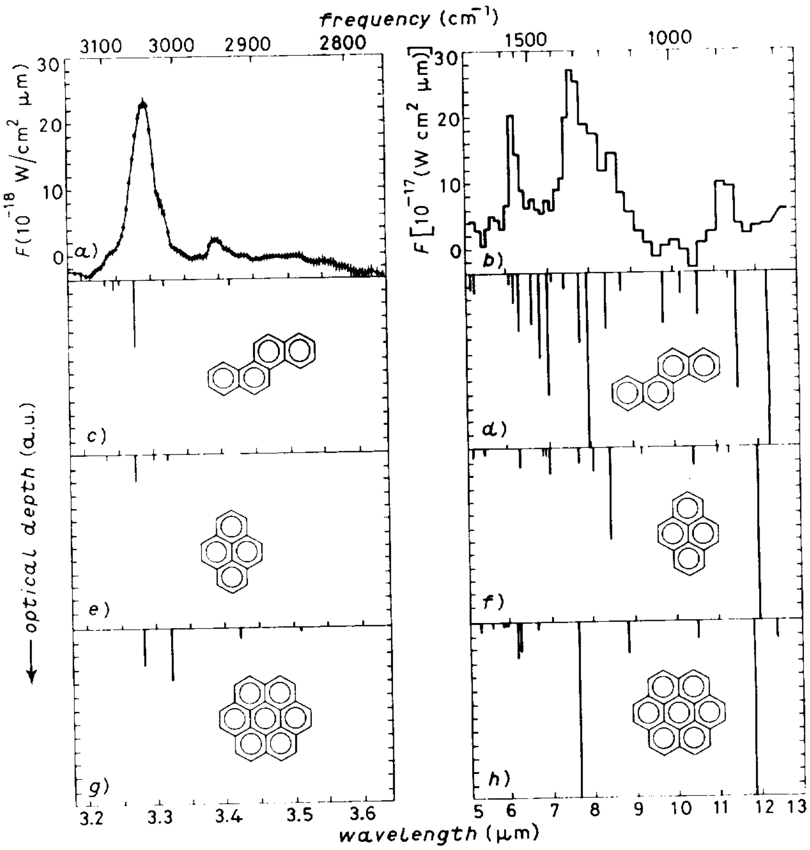

Fig. 3. – The $(3000 \div 770)\,\text{cm}^{-1}$ $((3 \div 13)\,\mu\text{m})$ emission spectrum from the Orion Bar compared with the absorption spectra of the PAHs chrysene, pyrene and coronene suspended in KBr pellets. *a*), *b*) Orion emission; *c*), *d*) chrysene; *e*), *f*) pyrene; *g*), *h*) coronene. (Orion, ref. [39]; chrysene, ref. [43]; pyrene, ref. [42]; coronene, ref. [44].) A schematic representation for the absorption spectrum is used because the KBr pellet technique alters the spectrum compared to that of a free species.

of bands from different PAHs along the line of sight [13, 45]. A homogeneous linewidth of $30\,\text{cm}^{-1}$ implies a redistribution time of about 0.2 ps, a value consistent with the vibrational-energy distribution time in other large molecules [46, 47]. It has recently been found that the band is narrower than shown in fig. 2 by nearly a factor of two in the high-flux vicinity of the star HD 44179 [48].

2·1.2. The minor bands in the $(3200 \div 2700)\,\text{cm}^{-1}$ $((3.125 \div 3.704)\,\mu\text{m})$ region. – There are a number of weak bands in this region. Unresolved shoulders straddle the major band at about 3085 and $2995\,\text{cm}^{-1}$ (3.24 and $3.34\,\mu\text{m}$) (see fig. 1*a*), 2*a*) and 3*a*)). These fall in the range generally assigned to overtones and combination bands involving CC stretching fundamentals in the

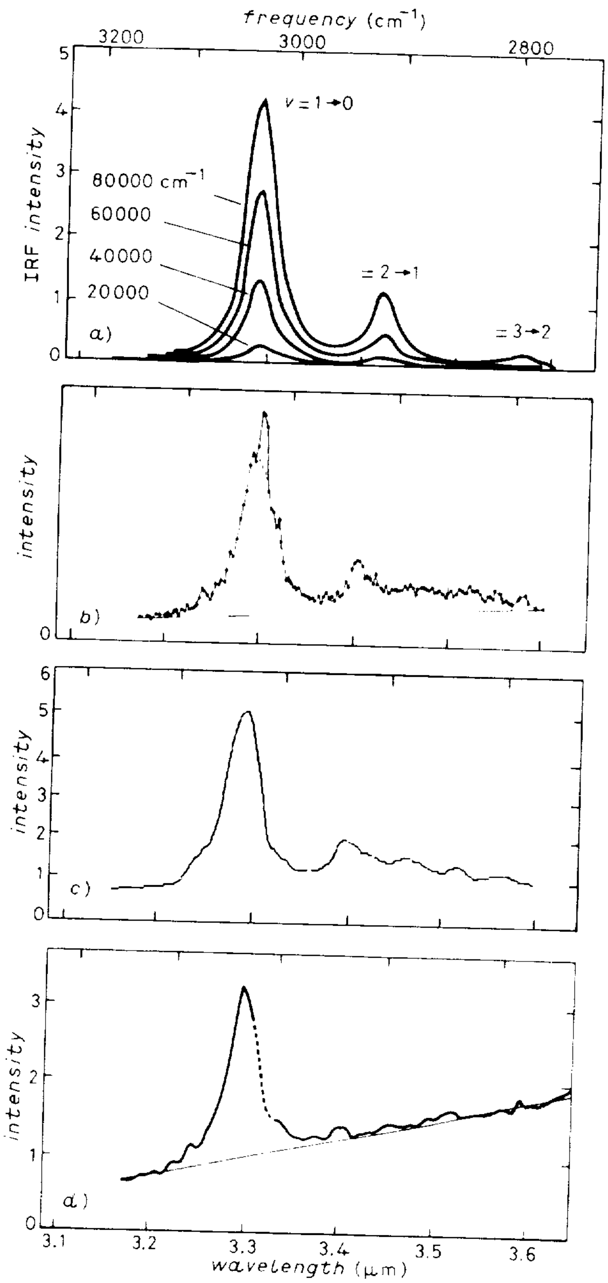

Fig. 4. – *a*) The calculated emission spectrum for chrysene in the CH stretching region as a function of vibrational-energy content. Anharmonicity is assumed to be 120 cm^{-1}. The observed emission spectra of *b*) NGC 7027 [36], *c*) IRAS 21282 + 5050 [49] and *d*) HD 44179 [38] showing how emission from higher vibrational levels depends on the availability of energetic photons. In NGC 7027, where the most energetic pumping photons are available, infrared emission from higher levels is important and produces a prominent $v =$ $= 2 \rightarrow v = 1$ band, whereas, in the relatively benign HD 44179, emission from $v = 2$ is barely discernible.

$(1810 \div 1050)\,\mathrm{cm}^{-1}$ ($(5.53 \div 9.52)\,\mu\mathrm{m}$) region and are responsible for most of the weak absorptions in fig. 3*c*), *e*) and *g*) [41-44]. These features should always be present in emission when the $3050\,\mathrm{cm}^{-1}$ ($3.28\,\mu\mathrm{m}$) band is intense because any species with enough internal energy to populate the fundamental at $3050\,\mathrm{cm}^{-1}$ ($3.28\,\mu\mathrm{m}$) contains enough energy to doubly populate the C-C stretching fundamentals. Fermi resonances between these different modes will certainly contribute as well. Many objects show a clear, weak band at about $2940\,\mathrm{cm}^{-1}$ ($3.4\,\mu\mathrm{m}$) [38], and weaker bands have recently been discovered at 2890, 2845 and $2805\,\mathrm{cm}^{-1}$ (3.460, 3.515 and $3.565\,\mu\mathrm{m}$) [49]. We have attributed the $2940\,\mathrm{cm}^{-1}$ band and some of the other weak features to the $(v = 1) \leftarrow (v = 2)$ aromatic CH stretch transition [45], although others have argued that it is carried by methyl ($—CH_3$), methylene ($—CH_2—$) and perhaps aldehydic (—HCO) side groups on PAHs [49]. Within the framework of the anharmonicity picture, fig. 4 shows that the prominence of the $2940\,\mathrm{cm}^{-1}$ ($3.4\,\mu\mathrm{m}$) band is directly related to the vibrational-energy content of the emitter. Thus anharmonicity can account for the presence of a band at about this frequency as well as the observation that it is most prominent in high-excitation objects such as NGC 7027 and on the ionization ridge in the Orion Nebula (fig. 3*a*)). Since the ultraviolet exciting spectrum can be characterized in several astronomical objects, the dependence on energy content can be used to deduce the size range of the species which dominate the emission. Analysis of the observed 3050 to $2940\,\mathrm{cm}^{-1}$ (3.28 to $3.4\,\mu\mathrm{m}$) intensity ratios show that PAHs containing between 20 and 30 carbon atoms dominate the emission in this region [45]. The corresponding $(v = 2) \leftarrow (v = 3)$ CH stretch transition is expected to fall at about $2800\,\mathrm{cm}^{-1}$ ($3.57\,\mu\mathrm{m}$). The spectra taken at several positions around the ionization ridge in the Orion Nebula (see fig. 5) show that the 2940 and $2850\,\mathrm{cm}^{-1}$ (3.4 and $3.5\,\mu\mathrm{m}$) band intensities vary with respect to the major band at $3050\,\mathrm{cm}^{-1}$ ($3.28\,\mu\mathrm{m}$) in a way which is consistent with the emission originating from upper CH stretch vibrational levels [50].

Naturally, the bands in this region may well represent a blend of the $(v = 1) \leftarrow (v = 2)$ and $(v = 2) \leftarrow (v = 3)$ aromatic CH stretching transitions with overtones and combinations involving aromatic CC stretches as well as aliphatic CH stretches. Many PAHs which do not have aliphatic side groups show weak absorptions near these frequencies. For example, fig. 6 shows that chrysene, pyrene and coronene all show substructure on a broad component. Chrysene and coronene show «peaks» at about 2910 and $2845\,\mathrm{cm}^{-1}$ (3.44 and $3.51\,\mu\mathrm{m}$), while pyrene has a broad (weak) plateau from 2950 to $2880\,\mathrm{cm}^{-1}$ (3.39 to $3.47\,\mu\mathrm{m}$) (which is similar to the emission plateau observed from the astronomical object BD + 30° 3639 [38]). In the laboratory spectra these are due to overtone and combination bands which have been perturbed sufficiently by solid-state effects to absorb weakly [40-44]. The perturbations within the PAH clusters that are suspended in salt pellets induce IR activity and broaden the individual bands causing them to overlap. In free vibrationally excited PAHs, perhaps Fermi

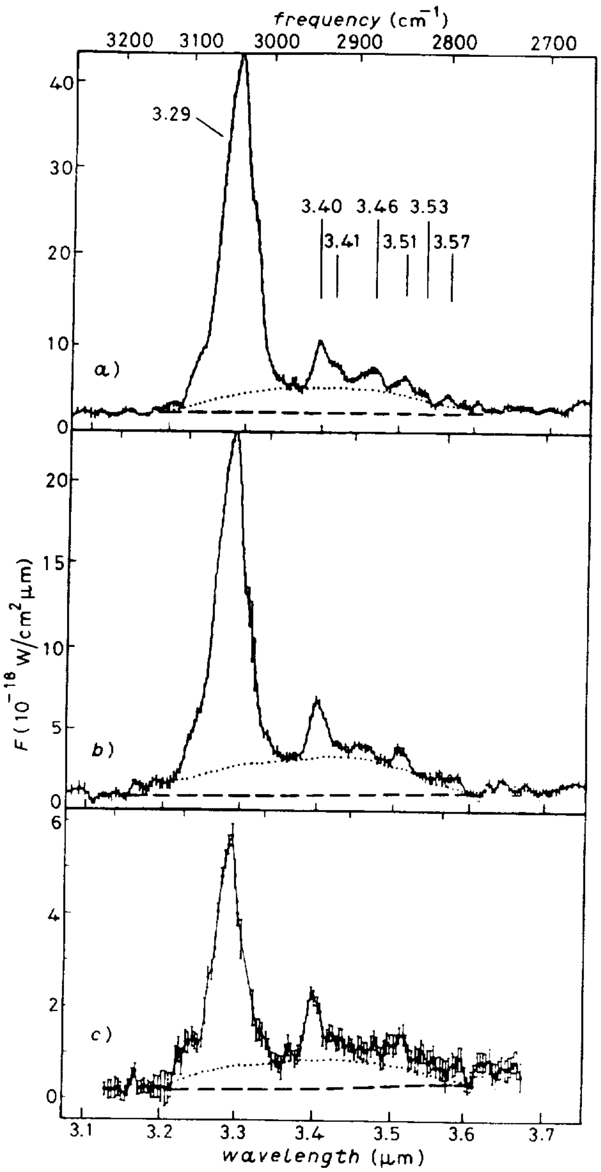

Fig. 5. – Spectra in the $(3200 \div 2700)\,\text{cm}^{-1}$ $((3.1 \div 3.7)\,\mu\text{m})$ range taken in a 5 arcsecond beam at three locations near the ionization ridge in the Orion Nebula. Position 4 (*a*)) is on the ridge between the ionized gas (H II region) and the neutral molecular cloud, while the positions 10 (*b*)) and 20 (*c*)) arcseconds south are within the molecular cloud. The dotted lines indicate the broad component, the dashed line the presumed continuum. Wavelengths, in μm, of the features are indicated in the top panel. Figure is from ref. [50].

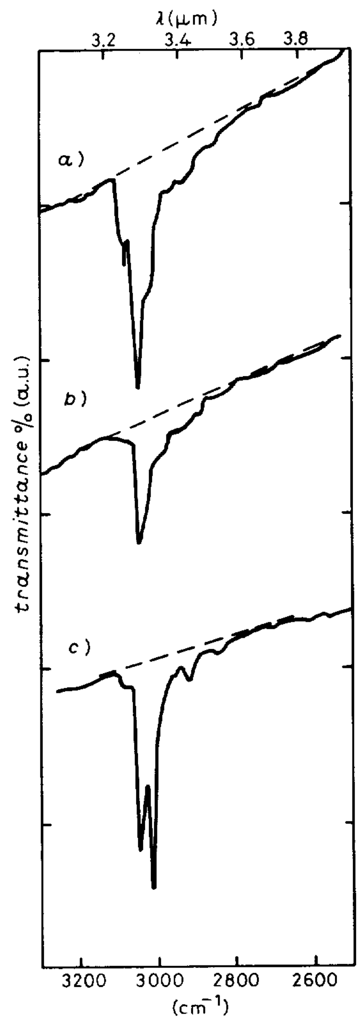

Fig. 6. – Infrared absorption spectra in the 3000 cm^{-1} (3.3 μm) region of the PAHs *a*) chrysene, *b*) pyrene and *c*) coronene, suspended in KBr. Spectra courtesy of Drs. B. N. CYVIN and P. KLAEBOE, University of Trondheim, Norway. Figure reproduced from ref. [17].

resonances between the overtones and combinations of CC stretching vibrations with the highly excited CH modes can sufficiently enhance the intensities of these presumably weak bands to produce the observed intensities.

2'1.3. The broad component in the $(3200 \div 2700)\,\text{cm}^{-1}$ $((3.125 \div 3.704)\,\mu\text{m})$ region. – Inspection of fig. 1, 3*a*), 4 and 5 shows that there is a broad component which stretches from about 3130 cm^{-1} to 2750 cm^{-1} $((3.19 \div 3.64)\,\mu\text{m})$. We have assigned this to a vibrational quasi-continuum produced by the overlapping of the different transitions discussed in the previous section: highly excited aromatic CH stretching vibrations, overtones and combinations of CC stretching vibrations and perhaps CH stretches on aliphatic side groups [14]. The spatial behaviour of the intensity of this broad component appears to follow the distribution of the major and minor bands in this region, rather than the distribution of the lower-frequency, broad features (discussed in subsect. 2.2.3 and 2.3.3) which are due to much larger PAHs and perhaps PAH clusters and amorphous carbon particles [39]. Thus this broad component is most likely due to molecule-sized free PAHs.

2.2. *The* $(2000 \div 1000)\,\mathrm{cm}^{-1}$ $((5 \div 10)\,\mu\mathrm{m})$ *region.*

2.2.1. The 1610, «1350» and $1150\,\mathrm{cm}^{-1}$ (6.2, «7.7», $8.7\,\mu\mathrm{m}$) major bands. – LEGER and PUGET pointed out that the frequency of the $1610\,\mathrm{cm}^{-1}$ ($6.2\,\mu\mathrm{m}$) band is as characteristic of polycyclic aromatic hydrocarbons as is the $3050\,\mathrm{cm}^{-1}$ ($3.28\,\mu\mathrm{m}$) band and attributed it to an aromatic C—C stretching fundamental [12]. As with the $3050\,\mathrm{cm}^{-1}$ ($3.28\,\mu\mathrm{m}$) band, the approximately $30\,\mathrm{cm}^{-1}$ width probably reflects vibrational-energy redistribution times within the molecules contributing to this band rather than a blending of narrower lines from different molecules. Some interstellar spectra show a slight asymmetry on the low-frequency side of this feature (*e.g.*, see fig. 3*b*) and ref. [16, 51]). This is suggestive of a contribution of emission from higher vibrational levels. As the anharmonicity of the C—C stretch is thought to be smaller than the natural bandwidth (a few cm^{-1} *vs.* $30\,\mathrm{cm}^{-1}$), blending should skew the band to lower frequencies [45].

The peak position and profile of the very broad «1310» cm^{-1} («7.7» μm) band, on the other hand, vary from object to object and their assignment has been correspondingly less straightforward. We assigned this band to the aromatic CC stretching vibrations for the following reasons [13]. The variation is consistent with PAHs since the frequency range across the base of the interstellar feature encompasses the frequencies expected for the strongest IR-active C—C stretching modes in a mixture of PAHs (*e.g.*, see fig. 3*d*), *f*) and *h*)). Unlike the 3050 and $1610\,\mathrm{cm}^{-1}$ (3.28 and $6.2\,\mu\mathrm{m}$) bands which consistently occur at nearly the same frequency in different aromatic molecules, the precise positions of these other IR-active aromatic C—C stretches depend on the molecule. Figure 3 shows that chrysene, pyrene and coronene have several strong C—C stretching bands in the region. As molecule size, degree of ring condensation and symmetry increase, the relative intensities of the 1610 and $1460\,\mathrm{cm}^{-1}$ (6.2 and $6.85\,\mu\mathrm{m}$) bands seem to reverse. Thus, if the interstellar mixture were complex enough, its IR spectrum in this region would show a broad feature, possibly exhibiting some substructure.

In the interstellar medium less stable PAHs will be weeded out, leaving a mixture dominated by the most stable structures [18, 20]. These more stable

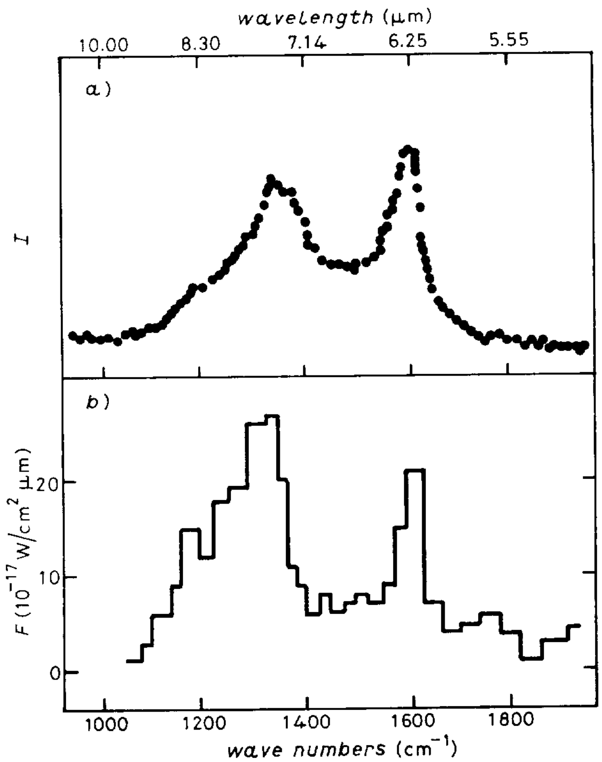

Fig. 7. – Comparison of the (2000 ÷ 1000) cm^{-1} (equivalent to the 5 to 10 μm region) Raman spectrum of auto soot (*a*))(a form of amorphous carbon which is rich in the more stable PAHs) with the emission from Orion (*b*)) (soot spectrum, adapted from ref. [52], Orion from ref. [39]). Figure from ref. [13].

PAHs are those which are symmetric and generally in the most condensed forms. An example of a mixture comprised largely of the most stable molecular forms is the soot produced in the high-temperature combustion of hydrocarbons. A comparison of the Raman spectrum in the (2000 ÷ 1000) cm^{-1} ((5 ÷ 10) μm) region of auto soot with the interstellar IR emission spectrum from Orion is shown in fig. 7. The Raman spectrum of soot principally probes the aromatic C—C stretching vibrational frequencies in this material because the Raman scattering cross-section for these bonds is very large and they are the most dominant type of bond in the mixture. Of course, for free PAHs with an inversion center of symmetry the infrared and Raman-active modes will be mutually exclusive. However, the perturbations in the soot particles break down the symmetry selection rules and the IR and Raman spectra become similar, as shown by comparing the IR spectra of high-temperature carbonaceous materials in ref. [23] and [53] with the Raman spectrum shown in fig. 7. Figure 7 dramatically shows that the distribution of the C—C stretching frequencies in

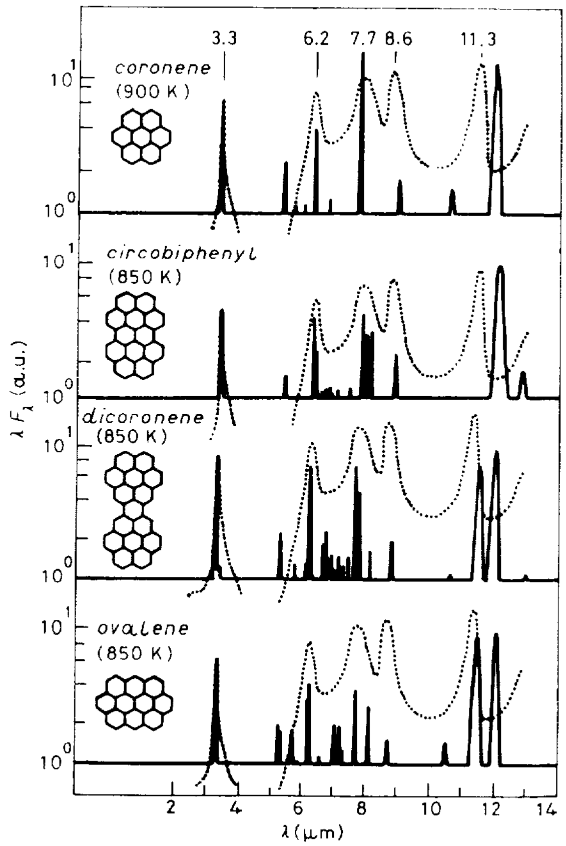

Fig. 8. – Emission spectra of several compact PAHs *calculated* from their absorption spectra measured in the laboratory at room temperature compared to the observed spectrum of the reflection nebula NGC 2023 (dots). Figure reproduced from ref. [54].

a mixture of the more stable PAHs coincides quite well with the frequency range of the major interstellar emission bands in the $(2000 \div 1000)\,\mathrm{cm}^{-1}$ $((5 \div 10)\,\mu\mathrm{m})$ region [13]. Assignment of the «1310» cm^{-1} («7.7» μm) interstellar feature to vibrations in symmetric interstellar PAHs is supported by the good agreement of the interstellar emission spectrum from the reflection nebula NGC 2023 with the infrared emission calculated from the measured absorption spectra of four symmetric PAHs shown in fig. 8 [54].

Finally, a band near $1150\,\mathrm{cm}^{-1}$ (8.7 μm) often appears as a small shoulder to the broad «1310» cm^{-1} («7.7» μm) feature but is resolved in certain objects (fig. 1 and 3*b*)). It has been assigned to the in-plane aromatic CH bending vibration [12].

Summing up, the 1610 and «1310» cm^{-1} (6.2 and «7.7» μm) bands are indicative of aromatic hydrocarbons and have been assigned to the aromatic C—C stretch. The variability of the peak position and profile of the «1310» cm^{-1}

(«7.7» μm) feature implies further that symmetric PAHs dominate the interstellar mixture. These are, of course, the most stable members of the PAH family.

2'2.2. The minor bands in the $(2000 \div 1000)\,cm^{-1}$ $((5 \div 10)\,\mu m)$ region. – There are three minor emission bands at about 1920, 1780 and $1460\,cm^{-1}$ (5.2, 5.62 and 6.8 μm) which have been associated with the interstellar emission spectrum. Emission in the $1900\,cm^{-1}$ (5.2 μm) region was searched for because nearly all laboratory PAH spectra show a weak band between 1960 and $1890\,cm^{-1}$ (5.1 and 5.3 μm). Based on this expectation, the spectrum of BD + 30° 3639 was measured in the $(2000 \div 1500)\,cm^{-1}$ $((5 \div 6.6)\,\mu m)$ region (see fig. 9) and a new emission band at about $1900\,cm^{-1}$ (5.26 μm) was indeed found [55]. Inspection of previous spectra, which terminate at about $1900\,cm^{-1}$, shows that most start to turn up at about $1850\,cm^{-1}$ (5.4 μm), implying that most objects which emit the major features have a band at this position [16, 51]. The confirmation of this feature provides strong support for the PAH hypothesis. Although the mode assignment is not well established, consideration of the relative absorption band strengths in previously published spectra and the symmetry assignments suggest that this is a combination (or overtone?) of the CH bending modes.

The 1780 and $1460\,cm^{-1}$ (5.62 and 6.8 μm) band intensities are variable. They were initially recognized in the spectrum of NGC 7027 and attributed to the IR emission band system by Bregman *et al.* [56]. Weak correlations between these and the major bands in several objects confirm that they are part of the emission band family [16]. These bands can be seen in fig. 1 and 9. There are several

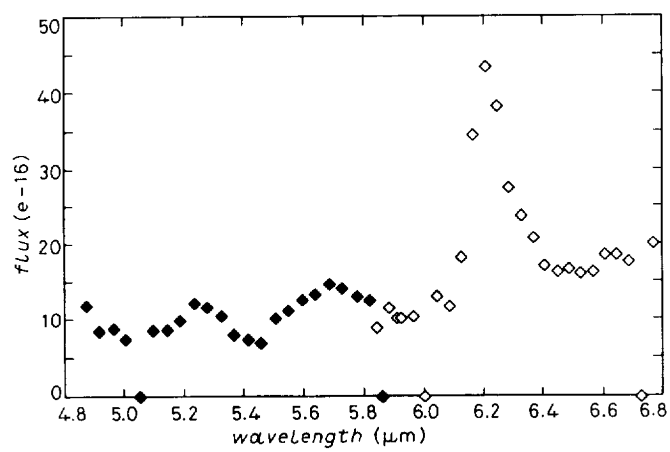

Fig. 9. – The $(2000 \div 1470)\,cm^{-1}$ $((5 \div 6.8)\,\mu m)$ spectrum of the planetary nebula BD + 30° 3639 showing the presence of a $1900\,cm^{-1}$ (5.2 μm) band. This spectrum was measured because nearly all laboratory spectra of PAHs show a band in the $(2000 \div 1850)\,cm^{-1}$ $((5 \div 5.4)\,\mu m)$ range. The detection of this feature gives strong support to the PAH hypothesis. Figure is from ref. [55].

possible assignments for the 1780 cm^{-1} (5.62 μm) band. It could correspond to one of the weaker PAH features such as shown in fig. 3*d*), *f*) and *h*), either as a weakly allowed C—C stretching fundamental or, as suggested by BREGMAN *et al.* [56], it may be an overtone of the major 890 cm^{-1} (11.2 μm) band. Alternatively, since this frequency is highly characteristic of the C=O stretch, it may arise from a carbonyl attached to a PAH or an interconnecting hydrocarbon chain. A carbonyl in the form of an aldehyde can be ruled out since there has been no detection of a prominent feature attributable to an aldehydic CH stretch near 2860 cm^{-1} (3.45 μm) in the objects which show a clear 1780 cm^{-1} (5.62 μm) band. Until the availability of both higher-resolution astronomical spectra (for more than a handful of objects) and laboratory spectra of suitable candidates, it will not be possible to determine which explanation is more likely.

The 1460 cm^{-1} (6.8 μm) band probably corresponds to an aromatic C—C stretching vibration (although it is conceivable that it may be an overtone or combination band involving C—H out-of-plane bending modes). Since only some PAHs absorb at this frequency (fig. 3*d*), *f*), *h*)), emission from a collection of PAHs could produce a relatively weak feature. Since the strength of this band depends strongly on the symmetry and geometry of the molecule, it may be a probe of the chemistry in the emitting region. An aliphatic CH deformation seems unlikely because, up to now, bands attributable to the aromatic CH stretching modes do not seem to correlate with the 1450 cm^{-1} (6.8 μm) band. Again, more observations are needed.

2·2.3. The broad component in the $(2000 \div 1000)$ cm^{-1} ($(5 \div 10)$ μm) region. – Inspection of fig. 1*b*) and 3*b*) clearly shows the presence of a broad, very roughly triangularly shaped, hump underlying the 1615 and 1300 cm^{-1} (6.2 and 7.7 μm) bands. This broad component is also evident in the spectra of other objects [16, 51]. As discussed in subsect. 2·2.1, this feature encompasses the region in which the IR-active, CC stretching modes in PAHs are richest. For example, of the 72 normal modes in pyrene, 42 involve CC vibrations (59%), while, in ovalene, 90 of the 132 (68%) are purely CC in character. While a certain fraction of these modes are infrared inactive, or only weakly allowed, and many involve lower-frequency bending modes, it is clear that PAHs (and PAH clusters) possess many bands that can overlap and produce a broad feature in this region. In fact the spectra of amorphous carbon particles (mixtures of aromatic structural units) have a strong feature in this region [23, 33, 53].

The importance of this component in the interstellar emission spectrum depends on both the intensity (flux) and energy of the ultraviolet radiation field. In objects where very energetic photons are plentiful, such as in NGC 7027, larger PAHs and materials composed of several smaller PAHs clustered together (loosely or in small amorphous carbon particles) may be excited sufficiently to emit in this band with intensities comparable to the intensities of the discrete features emitted by isolated PAHs. In regions where the ultraviolet radiation field is less intense and less energetic, such as in many reflection nebulae with much cooler exciting stars, small molecules can survive and their emission features tend to dominate the spectrum. The observed variability in intensity of this band with respect to the major band intensities is consistent with an origin in C—C vibrations in larger PAHs, PAH clusters and amorphous carbon particles containing on the order of 500 carbon atoms [17, 39].

In conclusion, the $(2000 \div 1000)\,\mathrm{cm}^{-1}$ ($(5 \div 10)\,\mu\mathrm{m}$) region of the interstellar emission spectrum can have two important contributors—free PAHs and small amorphous carbon particles or clusters of PAHs.

2'3. *The* $(1000 \div 500)\,\mathrm{cm}^{-1}$ ($(10 \div 20)\,\mu\mathrm{m}$) *region*.

2'3.1. The $890\,\mathrm{cm}^{-1}$ ($11.2\,\mu\mathrm{m}$) major band. – Until recently, the only feature in this region believed to be associated with the other emission bands was the prominent $890\,\mathrm{cm}^{-1}$ ($11.2\,\mu\mathrm{m}$) band shown in fig. 1, 2, 3 and 10. This was assigned to the out-of-plane aromatic CH bending vibration by DULEY and WILLIAMS in 1981 [11]. This, along with the $3050\,\mathrm{cm}^{-1}$ ($3.28\,\mu\mathrm{m}$) band, provided the original basis for an aromatic explanation of the interstellar emission bands. The $890\,\mathrm{cm}^{-1}$ ($8.2\,\mu\mathrm{m}$) band is skewed to lower frequencies in most emission spectra. This implies that emission from higher vibrational levels contributes to the observed band [45]. For highly vibrationally excited molecules the band will be quite asymmetric, broader and peaked at slightly lower frequencies than that from molecules containing less vibrational energy. The prominence of the band implied that the aromatic carriers be only partially hydrogenated since IR activity at $890\,\mathrm{cm}^{-1}$ ($11.2\,\mu\mathrm{m}$) is characteristic of aromatic systems with edge rings which contain only isolated, nonadjacent peripheral hydrogen atoms [41]. Fully hydrogenated PAHs possess several strong bands in the $(900 \div 500)\,\mathrm{cm}^{-1}$ ($(11 \div 20)\,\mu\mathrm{m}$) region. Partial hydrogenation is unexpected because hydrogen is more than 10^7 times more abundant than the proposed PAHs. This apparent inconsistency was resolved by the results described in the next two subsections.

2'3.2. The minor bands in the $(1000 \div 500)\,\mathrm{cm}^{-1}$ ($(10 \div 20)\,\mu\mathrm{m}$) region. – Quite recently weak, resolvable substructure has been detected at about 840 and $780\,\mathrm{cm}^{-1}$ (11.9 and $12.8\,\mu\mathrm{m}$) [57, 58]. These new bands are just where one would expect to find them for PAHs with doubly and triply adjacent H atoms per edge ring, relieving somewhat the constraint of partial dehydrogenation. As discussed in the next subsection, these new bands can be used to place important constraints on the moleculer geometries of the emitting PAHs. As with some of the minor bands in the $(3000 \div 2500)\,\mathrm{cm}^{-1}$ ($(3.3 \div 4)\,\mu\mathrm{m}$) region, the intensities of the 840 and $780\,\mathrm{cm}^{-1}$ (11.9 and $12.8\,\mu\mathrm{m}$) bands vary across the ionization ridge in the Orion Nebula (fig. 11), suggesting that certain PAHs may be particularly favored under the conditions which prevail in that region [58].

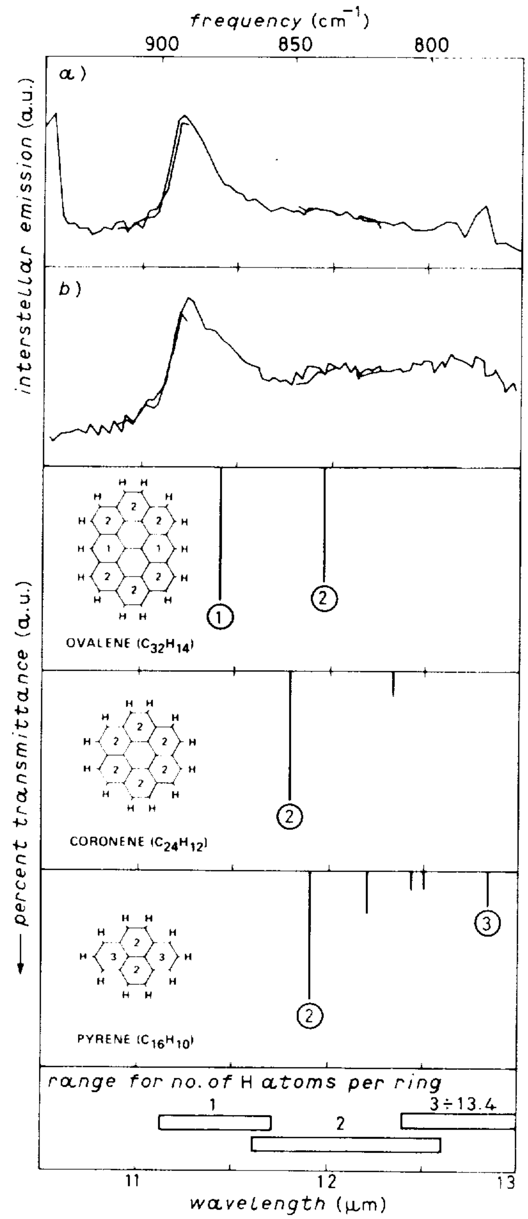

Fig. 10. – Comparison between the (940 ÷ 770) cm^{-1} ((10.5 ÷ 13) μm) emission spectra from *a*) NGC 7027 and *b*) IRAS 21282 + 5050 with schematic absorption spectra of PAHs in salt pellets. The PAHs shown contain isolated as well as doubly and triply adjacent H atoms on their peripheral rings. Figure from ref. [58].

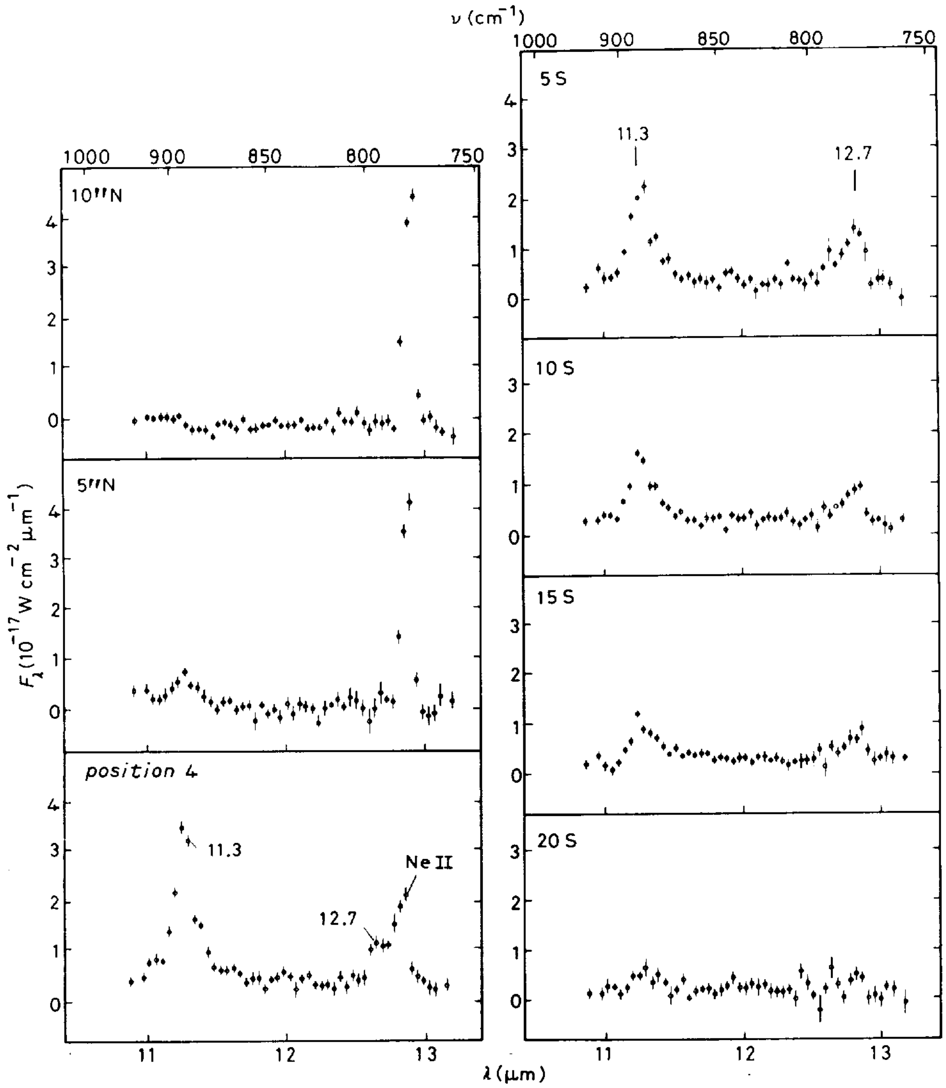

Fig. 11. – Spectra between 920 and 770 cm^{-1} ((10.9 ÷ 13) μm) from 10 arcseconds north to 20 arcseconds south of position four on the ionization ridge in the Orion Nebula. Positions 4, 10 S and 20 S are the same as the positions for the spectra shown in fig. 5. Figure from ref. [57].

The relative intensities of these bands pose several questions. If one assumes that the integrated absorbance per H atom is comparable for single as well as doubly and triply adjacent H atoms per edge ring, then one is still faced with a surprisingly large fraction of partially dehydrogenated PAHs. Detailed analysis of what this means in terms of the interstellar medium must wait until one has reliable band strengths for these different types of peripheral hydrogen atoms in isolated PAHs. Furthermore, the interstellar $(950 \div 770)\,\mathrm{cm}^{-1}$ $((10.5 \div 13)\,\mu\mathrm{m})$ broad component (discussed in the next subsection) and the $890\,\mathrm{cm}^{-1}$ $(11.2\,\mu\mathrm{m})$ band are generally much less intense than the «1310» cm^{-1} («7.7» μm) feature, whereas the opposite is true in the laboratory spectra. This later discrepancy has been shown to be the result of a spectral artifact produced by the techniques used to measure most of the PAH spectra published to date. Most laboratory spectra are obtained by mixing PAH crystallites with salt and pressing the mixture into a transparent pellet. Individual PAH molecules are not isolated in this way. Molecular interactions between adjacent PAHs produce large band strength enhancements in the $(900 \div 500)\,\mathrm{cm}^{-1}$ $((11 \div 20)\,\mu\mathrm{m})$ regions [59].

This property is not only important because it reconciles an apparently serious inconsistency with the PAH hypothesis but also because it provides a powerful spectroscopic argument in favor of the well-defined bands arising from free, molecule-sized species rather than particles (in which interactions would be expected to enhance emission in this region).

2·3.3. The broad component in the $(1000 \div 500)\,\mathrm{cm}^{-1}$ $((10 \div 20)\,\mu\mathrm{m})$ region. – Figure 12 shows the broad plateau of emission which extends from about 950 to $770\,\mathrm{cm}^{-1}$ $((10.5 \div 13)\,\mu\mathrm{m})$ that is evident in the spectra of objects that produce the IR emission bands. Because of the onset of telluric obfuscation at frequencies below about $800\,\mathrm{cm}^{-1}$ $(12.5\,\mu\mathrm{m})$ this plateau was not recognized until the launch of the Infrared Astronomical Satellite (IRAS) which measured very-low-resolution spectra from about 1000 to $300\,\mathrm{cm}^{-1}$ $((10 \div 330)\,\mu\mathrm{m})$. This observation relieved the difficulty associated with proposing only partial hydrogenation in exceedingly hydrogen-rich environments because it showed that the edge rings of the PAHs responsible for the features can have nonadjacent as well as 2 or 3 adjacent peripheral H atoms, but not 4 or 5. As mentioned above, this placed strong, important constraints on the molecular geometries of the aromatic hydrocarbons. These constraints are consistent with the conclusion drawn earlier (from the position and profile of the «1310» cm^{-1} («7.7» μm) band) that the most condensed, stable PAHs dominate the interstellar mixture [60].

2·4. *The far infrared.* – Skeletal vibrations such as C—C—C bending and ring puckering modes fall in the far IR. Figure 13 shows that a mixture of PAHs could produce a broad component composed of overlapping individual lines in the $(625 \div 330)\,\mathrm{cm}^{-1}$ $((16 \div 30)\,\mu\mathrm{m})$ range. From the limited information available, it seems that these bands are at least a factor of two weaker than the mid-IR bands (although this may be an artifact produced by the steric constraints placed on such collective large molecule vibrations by the solid matrix). Objects showing the PAH mid-IR bands should also have broad, low-level emission extending out to about $330\,\mathrm{cm}^{-1}$ $(30\,\mu\mathrm{m})$. At lower frequencies the positions be-

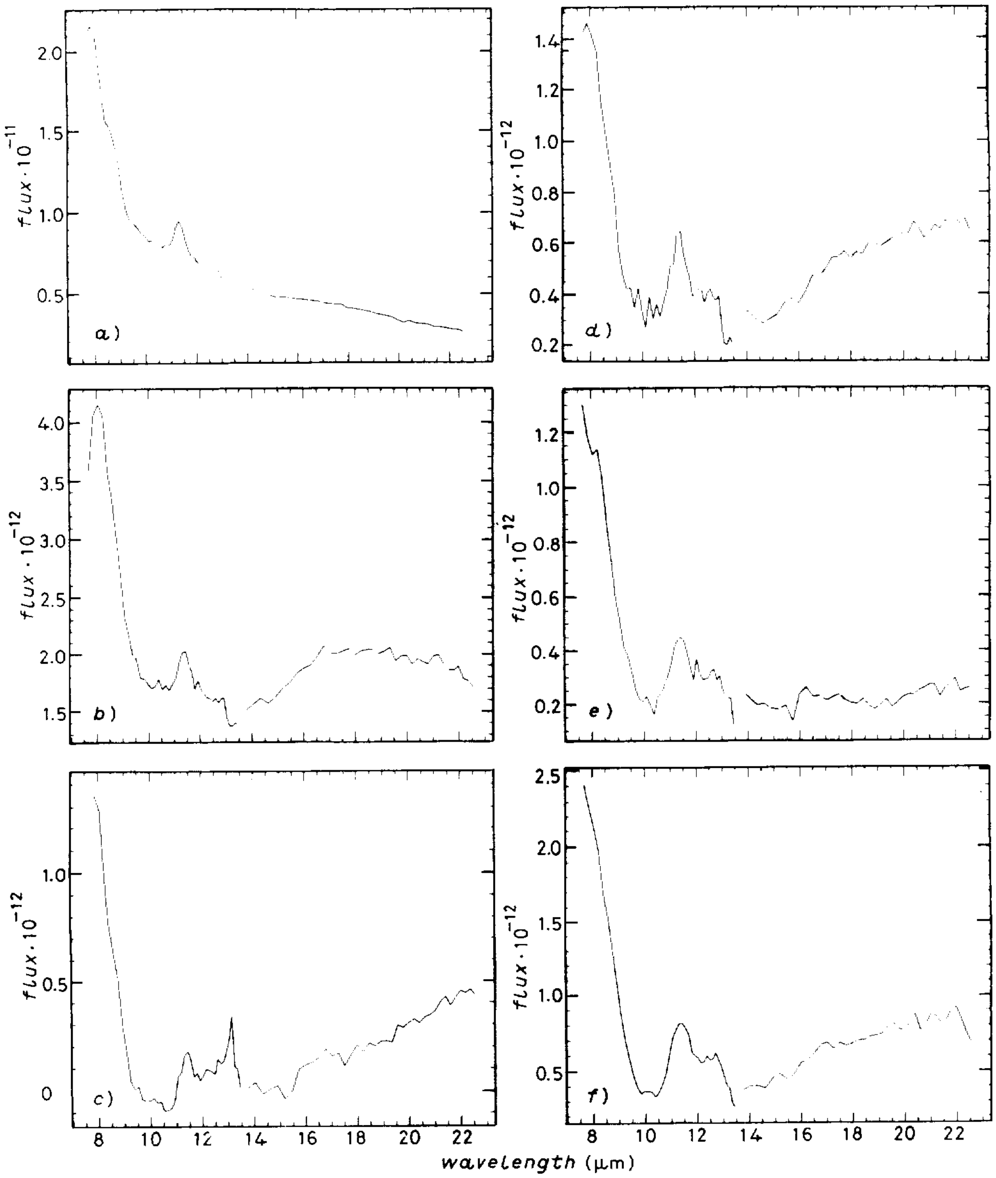

Fig. 12. – The LRS (Low Resolution Spectrometer) spectra of six IRAS sources: *a*) HD 44179, *b*) HEN 1044, *c*) 17199 – 3446, *d*) P 18, *e*) 06114 + 1745, *f*) 20319 + 3958. The short-wavelength data span the range from 1300 to 740 cm^{-1} ((7.67 ÷ 13.45) μm). The long-wavelength data are shown from 730 to 450 cm^{-1} (13.72 to 22.55 μm). The «1310» («7.7» μm) feature dominates the high-frequency end of these spectra. The 890 cm^{-1} (11.2 μm) band shows a long-wavelength plateau extending to about 770 cm^{-1} (13.0 μm). Ordinates are flux in W m^{-2} μm^{-1}. Figure from ref. [60].

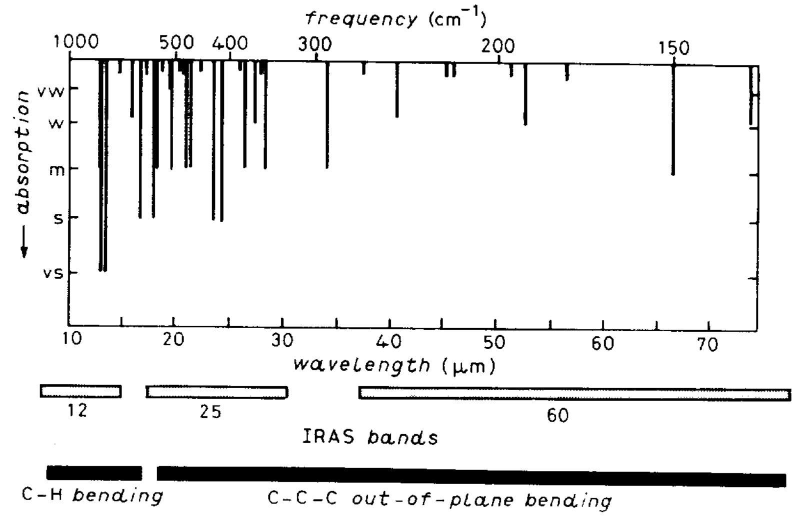

Fig. 13. – A schematic composite absorption spectrum for the out-of-plane vibrations in a mixture of the aromatic molecules naphthalene, chrysene, pyrene and coronene in the $(1000 \div 130)\,cm^{-1}$ $((10 \div 77)\,\mu m)$ range compared to the IRAS bands. The regions in which the CH in- and out-of-plane and carbon plane bending vibrations fall are also indicated.

come rather molecule specific. These bands may well be responsible for the emission associated with reflection nebulae and high-galactic-latitude clouds discovered by the IRAS satellite in broad spectral bands centered at 12 and $25\,\mu m$ [6, 13, 21, 61].

The intensity of the $12\,\mu m$ IRAS band drops with respect to that of the $25\,\mu m$ band in the vicinity of the exciting star in the case of reflection nebulae [62] and close to hot stars in the case of the high-galactic-latitude clouds [63]. If PAHs and PAH-related materials are responsible for the emission, this behavior can be understood in terms of dehydrogenation rather than grain destruction as previously suggested. As shown in fig. 13, the $12\,\mu m$ IRAS band covers the $(1250 \div 670)\,cm^{-1}$ $((8 \div 15)\,\mu m)$ range which primarily encompasses the CH in-plane and out-of-plane bending vibrations in PAHs, while the $25\,\mu m$ IRAS band covers the $(560 \div 330)\,cm^{-1}$ $((18 \div 30)\,\mu m)$ region which encompasses the C—C—C aromatic, plane bending vibrations of PAHs. Consequently, if a PAH is stripped of hydrogen, it will lose most of its IR activity in the $(1000 \div 600)\,cm^{-1}$ $((10 \div 16.7)\,\mu m)$ region but not in the $(600 \div 10)\,cm^{-1}$ $((16.7 \div 1000)\,\mu m)$ region. Small PAHs $(15 \div 30$ carbon atoms) contribute strongly to the infrared emission because they are the most highly vibrationally excited by the absorption of an ultraviolet photon. These are also the PAHs which will be the first to suffer H atom loss if sufficiently excited [17]. Consequently, if PAHs are indeed responsible for this emission, the drop in intensity of the $12\,\mu m$ IRAS band with respect to the $25\,\mu m$ IRAS band can be understood in terms of the dehydrogenation of the most intensely emitting PAHs and not the destruction of the carbon skeleton or of a particular class of grains. As with the other frequency regions, further progress in the far IR will require laboratory experimentation and theoretical development.

3. – Conclusions.

Many different celestial objects emit an infrared spectrum which has been attributed to a family of aromatic hydrocarbons. The emission is thought to arise from molecule-sized polycyclic aromatic hydrocarbons (PAHs) and related materials which have been highly vibrationally excited by the absorption of visible or ultraviolet photons. The most intense higher-frequency spectral features come primarily from species containing $20 \div 50$ carbon atoms. Larger species are certainly present as well. Given the same excitation conditions, the larger species probably make increasingly important contributions to the lower-frequency bands. There is some controversy over whether the smaller PAHs are free (*i.e.* in the gas phase) or structural units of amorphous carbon particles and PAH clusters. There is also evidence for the presence of substantially larger PAHs, PAH clusters and amorphous carbon particles containing on the order of 400 carbon atoms.

The spetroscopic assignments are based on a rough similarity between the interstellar spectra and laboratory spectra of PAHs and related materials. As the species in space are most likely in forms little studied in the laboratory, much experimental and theoretical work is called for on aromatic hydrocarbons. In the interstellar medium the proposed mixture includes species which are larger than many previously studied, ionized and dehydrogenated. Until the spectroscopic properties of these types of molecules are characterized, full advantage of the PAH model cannot be realized. This represents an important challenge as PAHs appear to be ubiquitous and abundant throughout the interstellar medium. They are probably more abundant than all of the other known interstellar polyatomic molecules combined. As such, they are potentially excellent probes of conditions in many different objects. They may also be the missing link between the carbon ejected from carbon-rich red giant stars and the carbon particle component of interstellar dust (and perhaps the carbon found in meteorites and interplanetary dust particles).

* * *

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